Supramolecular Polymers

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Supramolecular Porphyrin Copolymer Assembled through Host–Guest Interactions and Metal–Ligand Coordination

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Abstract: *Bisporphyrin cleft molecule* ***1 Zn*** *possessing a guest moiety assembled to form supramolecular polymers through host–guest interactions. Bispyridine cross-linkers created interchain connections among the supramolecular polymers to form networked polymers in solution. Solution viscometry confirmed that the cross-linked supramolecular polymers were highly entangled. Frequency-dependent linear viscoelastic spectroscopy revealed that the supramolecular polymers generated well-entangled solutions with associating and networking polymers, whereas the solid-like aggregates moved individually without breaking and reforming structures below the transition temperature of 9.6°C. Morphological transition of the supramolecular polymers was evidenced by AFM images; the non-cross-linked polymer resulted in wide-spread thin networks, while the cross-linked networks produced thicker worm-like nanostructures. The supramolecular networks gelled in 1,1,2,2-tetrachloroethane, and an elastic free-standing film was fabricated with a Young's modulus of 1 GPa.*

Supramolecular polymers have been innovatively developed in recent materials science.[1] Stimuli-responsiveness, self-healing, and easy fabrication are several fascinating features of supramolecular polymers, which exhibit a broad array of applications in material science. Thus, a great deal of effort has been devoted to the construction of advanced supramolecular polymer materials. Although a variety of noncovalent interactions, such as hydrogen bonding,[2] π-π stacking,[3] dipole-dipole,[4] host–guest interactions,[5] and their combinations[6] have been employed to construct supramolecular polymers, the low stability of noncovalent bonds may restrict the flexibility of supramolecular polymers in real applications owing to poor mechanical robustness. To compensate for this defect, linear supramolecular polymers composed of molecular monomers require increased supramolecular interactions; thus two or more types of binding sites in a monomer unit are employed. Network polymerization of the monomer produces supramolecular polymer networks that can provide the materials with macroscopic robustness.[7]

Supramolecular porphyrin polymers have attracted particular attention because of their unique optical and electronic properties. Coordination-driven self-assembly is one of the most useful approaches to construct large and elaborate porphyrin architectures.[8] By contrast, supramolecular porphyrin polymers that self-assemble through noncovalent interactions have been moderately reported.[9] We previously developed bisporphyrin clefts that create complementary dimers and host–guest complexes,[10] which have been utilized for supramolecular polymerization.[11] Heteroditopic monomer **1** ($M = H_2$) has been polymerized by a charge transfer interaction to yield supramolecular porphyrin polymers.[12] Placing a zinc metal ion in the porphyrin core can provide coordination sites (Scheme 1). Coordination-driven cross-linking should be an effective way to provide macroscopically robust supramolecular materials. However, there are limited examples of coordination and host–guest interaction sites participating in a cooperative fashion to produce supramolecular polymer networks.[13] Herein, we report supramolecular porphyrin polymer networks formed by coordination and host–guest interactions that result in entangled polymer solutions, even though each monomer remains connected by noncovalent bonds (Scheme 1).

The self-assembling behavior of **1Zn** was studied using absorption and fluorescence spectroscopies in chloroform. **1Zn** exhibited two well-defined fluorescence bands at 598 and 643 nm at 323 K, corresponding to the singlet–singlet Q_{0-0} and Q_{0-1} transitions of the ZnTPP group ($\lambda_{ex.} = 548$ nm), respectively.[14] Upon cooling the solution, the emission bands decreased, indicating that the trinitrofluorenone (TNF) moiety was captured within the bisporphyrin cleft. The absorption spectrum of **1Zn** was concentration-dependent in chloroform. The self-association constant K_E was determined using an isodesmic model to be $240000 \pm 40000\,\mathrm{L\,mol^{-1}}$ at 298 K, which was consistent with the intermolecular association constant (K_a: $200000 \pm 10000\,\mathrm{L\,mol^{-1}}$) between **2Zn** and 2,4,7-trinitrofluorenone.

Supramolecular cross-linking was confirmed by ^{1}H NMR titration with bispyridine **3**[15] in chloroform-d_1 (Figure 1). The aromatic signals of the TNF moiety of **1Zn** appeared at 7.10, 6.57, and 6.00 ppm with large upfield shifts higher than 1.6 ppm. The large upfield shifts suggested that the TNF moiety was placed within the bisporphyrin cleft, in which the aromatic protons experienced a strong shielding effect. Thus, the iterative host–guest complexation in a head-to-tail fashion resulted in supramolecular polymeric arrays. Upon adding **3**

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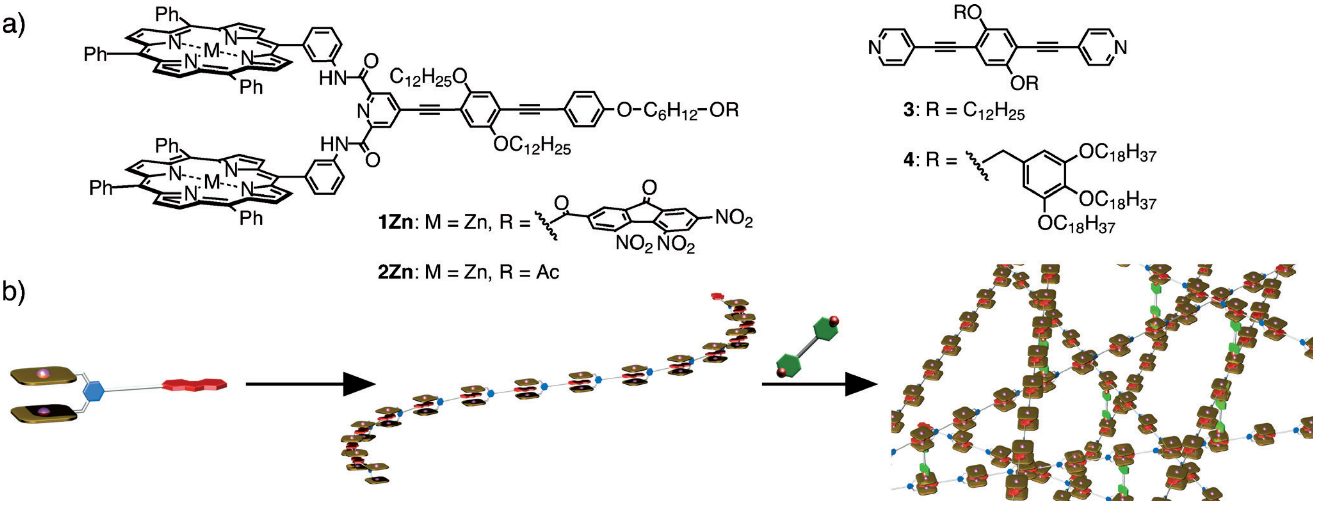

Scheme 1. a) Heteroditopic monomer **1Zn**; acetyl analogue **2Zn**; cross-linkers **3** and **4**; b) representation of supramolecular polymerization through host–guest interactions and ligand–metal coordination.

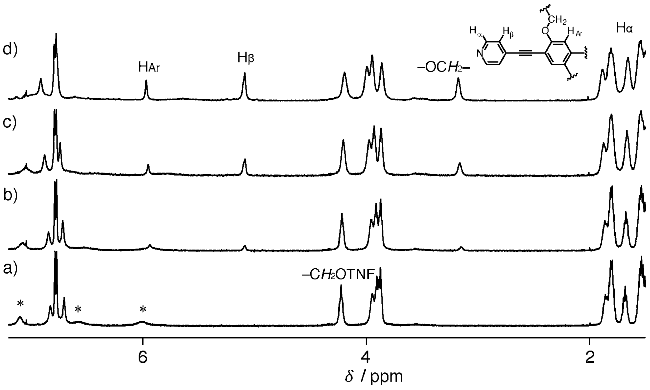

Figure 1. ^{1}H NMR spectra of **1Zn** (8.36 mmol L^{-1}) with a) 0.0, b) 0.1, c) 0.3, and d) 0.5 equiv of **3** in chloroform-d_1 at 298 K. Asterisks denote the TNF protons of **1Zn**.

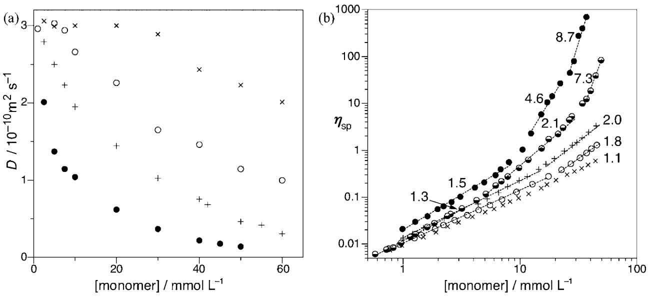

Figure 2. a) Diffusion coefficients of **1Zn** (○), **1Zn** with 0.5 equiv of **3** (●), **2Zn** (×), and **2Zn** with 1.0 equiv of **3** (+) in chloroform-d_1 at 297 K. b) Specific viscosities of **1Zn** (○), **1Zn** with 0.5 equiv of **4** (half-filled circle), **1Zn** with 1.0 equiv of **4** (●), **2Zn** (×), and **2Zn** with 1.0 equiv of **3** (+) in chloroform-d_1 at 293 K.

to the **1Zn** solution, the α- and β-pyridiyl protons, Ar-*H*, and ArOCH_2-, of **3** shifted upfield to 1.67, 5.09, 5.93, and 3.15 ppm with large complexation-induced shifts ($\Delta\delta = -6.94$, -2.30, -1.10, and -0.88 ppm, respectively), clearly indicating that the two zinc porphyrin rings were linked by **3**; consequently, the shielding effect of the zinc porphyrins was rationalized. The aromatic signals of the TNF moiety also moved farther upfield than those in the absence of **3**, implying that the intermolecular head-to-tail connection was stabilized. Accordingly, the coordination-driven cross-linkages participated in a cooperative fashion to stabilize the supramolecular polymeric networks by forming cross-linkages.

The size of molecular assemblies in solution is generally correlated with diffusion coefficients derived from diffusion-ordered NMR spectroscopy.[16] Diffusion coefficients for **1Zn** and **2Zn** in the presence and absence of cross-linker **3** in chloroform-d_1 were obtained at various concentrations using the bipolar pulse pair-stimulated echo (BPP-STE) method (Figure 2a). Diffusion coefficients (*D*s) for **2Zn** possessing the acetoxy tail were consistently less than 30 mmol L^{-1}. An average diffusion coefficient of $2.99(2)\times10^{-10}$ m^{2}s^{-1} was determined to be a monomeric form. Above this concentration, **2Zn** displayed slightly smaller *D*s. Bisporphyrins have been shown to form complementary dimeric structures; therefore, **2Zn** most likely formed a head-to-head dimeric structure in concentrated solutions.[10] Upon adding one equivalent of bispyridine ligand **3**, the diffusion coefficient for **2Zn** became concentration-dependent. The diffusion coefficient for **2Zn** was significantly decreased to $0.463(1)\times10^{-10}$ m^{2}s^{-1} when the concentration of **2Zn** reached 50 mmol L^{-1}. The coordination-driven polymerization of **2Zn** with **3** produced large polymeric aggregates in solution. The heteroditopic monomer **1Zn** polymerized in a head-to-tail fashion. At a diluted concentration lower than 7.5 mmol L^{-1}, an average *D* value of $2.99(5)\times10^{-10}$ m^{2}s^{-1} for **1Zn** was in good agreement with that given for **2Zn**, suggesting that **1Zn** existed as a monomer. At a concentration of 60 mmol L^{-1}, the *D* value for **1Zn** was decreased by more than 60%, clearly indicating that supramolecular polymerization of **1Zn** occurred above a critical polymerization concentration (CPC) of 7.5 mmol L^{-1}. Upon adding 0.5 equivalent of **3**, the D value for **1Zn** was appreciably decreased and reached $0.2182(6)\times10^{-10}\,\mathrm{m^2\,s^{-1}}$ at a concentration of 40 mmol L^{-1}. Cross-linking of the supramolecular polymeric aggregates of **1Zn** clearly facilitated the growth of the supramolecular polymeric networks.

The dynamics of the supramolecular polymer and its network in solution were discussed using viscometry. Specific viscosities (η_{sp}) for **1Zn** and **2Zn** in the presence and absence of cross-linkers **3** and **4**[17] were obtained using an Ubbelohde viscometer at various concentrations in chloroform at 293 K (Figure 2b). Double-logarithmic plots of the specific viscosities versus the concentrations of **1Zn** and **2Zn** yielded a good linear relationship below the CPC. At a lower concentration, both of the exponents for **1Zn** and **2Zn** without the cross-linkers were near unity, indicating that both of the solutions behave as Newtonian fluids. The transition from dilute to semidilute regions was only observed in the **1Zn** solution (CPC: 14.5 mmol L^{-1}). Above the CPC, the plots curved upward, reaching a slope of 1.8. Accordingly, a head-to-tail host–guest complexation drove the formation of the supramolecular polymeric aggregates of **1Zn**, in which the interchain interactions primarily contributed to the solution viscosity. Upon the addition of linker **3** to the solution of **2Zn**, monomeric **2Zn** became polymeric. The transition appeared at a CPC of 16.6 mmol L^{-1}, and a slope of 2.0 above the CPC suggested that the zinc–nitrogen coordination between **2Zn** and **3** effectively drives supramolecular polymerization. Accordingly, both the coordination bond and the host–guest interaction effectively promoted the formation of supramolecular polymeric aggregates.

Cross-linker **4** in the **1Zn** solution significantly changed the dynamics. The first transitions were observed at the CPCs of 5.6 and 9.0 mmol L^{-1} for **1Zn** with 0.5 and 1.0 equiv of **4**, respectively. These CPCs shifted to lower values than those observed without **4**. Above the CPCs, the plots curved upward with slopes of 2.1 and 4.6 with 0.5 and 1.0 equiv of **4**, respectively. The slopes were obviously correlated to the amount of **4**, suggesting that the coordination of **4** to the polymer chains of **1Zn** promoted polymer growth. Assuming that cross-linker **4** acted as a sticker, the first transitions were the overlapping concentration (c^*) of the sticky polymer based on the Rubinstein–Semenov model, leading to a scaling law exponent of 3.6 above the c^* closer to the gel point.[18] The gelation of **1Zn** occurred with 1.0 equiv of **4** above c^*. The second transitions were observed for **1Zn** with **4** in a higher concentration range. The exponents of **1Zn** were 7.3 and 8.7 with 0.5 and 1.0 equiv of **4**, respectively. These findings suggested that cross-linker **4** promoted the formation of highly entangled polymer networks, most likely obeying the sticky reptation regime with a predicted scaling law exponent of 6.78.

A dynamic viscoelastic study provided insights for wide-range dynamics of supramolecular polymer chains in solutions (Figure 3).[19] Frequency-dependent viscoelastic spectra of a **1Zn** solution (21.5 mmol L^{-1}) with 1.0 equivalent of **4** in 1,1,2,2-tetrachloroethane were measured at temperatures from 25 to 5 °C. The dynamic moduli (G' and G'') were measured as a function of the angular frequency, ω. The plots of G' and G'' versus ω showed characteristic dynamics of supramolecular polymer networks in solutions. Measured G' and G'' values were scaled as ω^2 and ω^1 at a low frequency higher than 15 °C (Figure 3a–c), and the results indicated that polymer chains relax with single terminal relaxation time. Owing to the stable response in the terminal relaxation region, the breaking and reforming dynamics of the non-covalent bonds were close to or faster than the lifetime of an equivalent unbreakable chain mode in associating polymers. Above the cross-over of G' and G'', the G' was larger than the G'' value, indicating that the relaxation process was faster than the rates of breaking and reforming noncovalent bonds, which were promoted until the transition of G'' occurred. In contrast, G'' was always larger than G' at 5 °C, and non-Maxwellian behavior was observed for G' in the measured frequency region (Figure 3d). Differential scanning calorimetry (DSC) measurements of the solution also produced the weak transition at 9.6 °C upon cooling. Accordingly, above the transition temperature, the supramolecular polymers generated the well-entangled solution with associating and networking polymers, whereas local chain relaxation was constrained below the transition temperature, leading to small solid-like aggregates that moved individually without breaking and reforming structures.

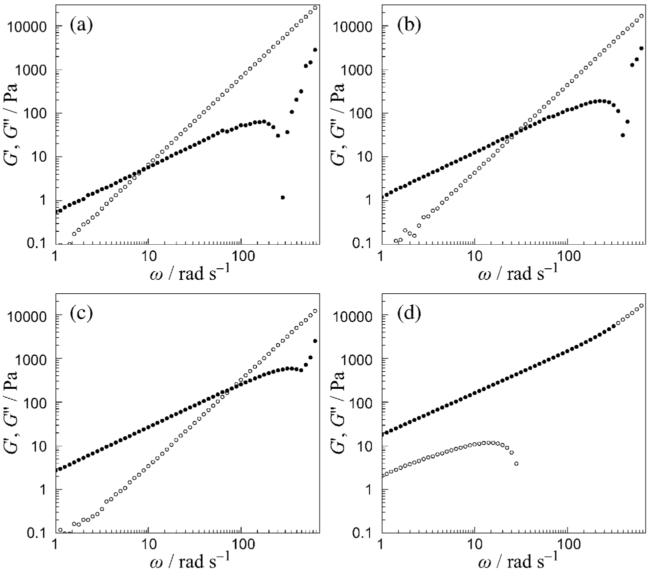

Figure 3. Frequency-dependent storage (G', open circles) and loss (G'', closed circles) moduli of **1Zn** (21.5 mmol L^{-1}) with 1.0 equiv of **4** in 1,1,2,2-tetrachloroethane at a) 25 °C, b) 20 °C, c) 15 °C, and d) 5 °C.

The terminal relaxation time τ_{d} of the supramolecular polymer networks corresponded to the intersection of G' and G'', which occurred above the transition temperature. The network relaxation time τ_{d} was dependent on temperature. Surprisingly, as the temperature was increased, the relaxation time τ_{d} shifted to lower frequencies, implying that the polymer chains intriguingly became longer. The relaxation modes were strongly influenced by the breaking and reforming of the non-covalent bonds that constituted the network chains, either the main chains or the network junctions, even though the two supramolecular bonds should have independently contributed to the polymer networks. Although these non-covalent bonds typically lasted less than the chain terminal relaxation time of the polymer networks, the well-developed polymer networks were most likely entangled, increasing the length of the bond lifetime owing to steric congestion at the non-covalent connection and junction of each monomer. These results provided a plausible picture that the supramolecular polymer chains were partially liberated from the solid-like aggregates above the transition temperature, leading to formation of the entangled polymer networks.

1Zn was soluble in 1,1,2,2,-tetrachloroethane and yielded a purple solution. Upon adding one equivalent of **4** to the solution, the solution became sticky, and the gel was formed (Figure 4a,b). The supramolecular polymer network was clearly responsible for gelation. The solution was cast on a Teflon sheet and dried for one day to produce free-standing film(Figure 4c). The film was elastic and could be bent by picking up one of the ends. When a weight of 15 g was loaded, the film maintained its shape. A Young's modulus of 1 GPa was measured by the stress–strain curve. The supramolecular polymer was mechanically robust.

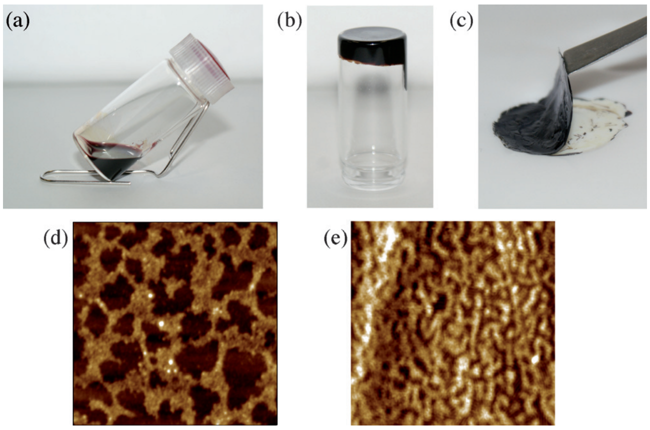

Figure 4. A solution of a) **1Zn** (18 wt%) and a gel of b) **1Zn** with 1 equiv of **4** (18 wt%) in 1,1,2,2,-tetrachloroethane. c) A free-standing film prepared from a chloroform solution of **1Zn** with 1 equiv of **4**. Atomic force microscopic images of d) **1Zn** (1×1 μm) and e) **1Zn** (0.5×0.5 μm) with 1 equiv of **4** on a mica surface.

The surface morphology of the supramolecular polymers of **1Zn** in the absence and presence of cross-linker **4** were observed by atomic force microscopy. Well-developed supramolecular polymer networks are shown in Figure 4d. The widely spread fibers that formed non-woven textile fabrics had a uniform height of 1.5 ± 0.1 nm, which closely matched that of the bisporphyrin moiety, implying that the porphyrin moieties adopted a parallel alignment in which the zinc center interacted with the oxygen functionalities on the mica surface. In contrast, a 1:1 solution of **1Zn** and **4** resulted in thicker worm-like nanostructures with heights of 1.2 ± 0.1 nm and widths of 26 ± 8 nm (Figure 4e). Accordingly, the metal coordination organized the uniform fibers, comprised of a bundle of supramolecular polymeric chains.

In summary, we demonstrated that the host–guest interaction-directed supramolecular polymers were cross-linked with metal–ligand coordination, resulting in supramolecular polymer networks. Diffusion-ordered NMR spectroscopy and viscometry of the polymer solution revealed that the host–guest interactions and coordination bonds participated in a cooperative fashion. The viscoelastic property of the polymer networks was confirmed by the rheological study. The supramolecular polymers generated a well-entangled solution with associating and networking polymers, whereas the solid-like aggregates moved individually without breaking and reforming structures below the transition temperature of 9.6 °C. The elastic free-standing polymer films with a Young's modulus of 1 GPa were fabricated. The supramolecular network copolymer, composed of the molecular monomers, is now a promising candidate for advanced supramolecular materials with macroscopic robustness that can be potentially utilized for self-healing applications.

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